

Evaluation of Peanut Shell, Bentonite Clay and its Composites in the Removal of Dye (Malachite Green) from Industrial Wastewater

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ABSTRACT

Curtailing the effects of environmental pollution being a major problem encountered by third-world countries, this study was embarked on to reduce the effect of land and water pollution caused by improper disposal of dye used by industries by using readily available agricultural waste like peanut shell, bentonite clay and its composite. Analysis that was used included Scanning electron microscope (SEM), Electron dispersive x-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR) Some physical parameters were considered too: Absorbent load, Contact time, pH and Concentration. The results from the SEM, EDX and FTIR showed the adsorptive capacities of the absorbents, it's functional and the compounds contained. The result of the physical parameters for adsorbent load; Peanut shell the percentage removal increase from 26.93%-28.0%. For bentonite clay increase from 7.05%-8.24%. The combination of both peanut shell and bentonite increased from 93.22%-95.40%. For the contact time the dye removal percentage increase from 99.13%-99.37% which later decreased to 98.16%. Bentonite clay decreased from 71.09%-69.53% and later increased to 70.13%. The combination decreased from 52.33%-51.29% and increased to 52.60% but decreased at the last lap to 50.83%. At 60-80 minutes optimal time was achieved due to saturation of active sites for high removal of dye efficiency. pH was observed too which varied. Peanut shell shows that the percentage removal increased from 61.89%-62.37% then decreased to 60.87%. Bentonite clay decreased from completely from 99.72%-97.58%. The combination decreased from 32.14%-31.94% then increased to 33.54%. We can say that for the peanut shell and the combination of both peanut shell and bentonite clay pH was increased slightly at the acidic side.

Keywords: Peanut shell, Bentonite clay, Malachachite green, Dye, Industrial waste

1.0. Introduction

Water pollution as a result of waste water from textile industry represents a great challenge, and activated carbon is a common adsorbent used to remove hazardous contaminants such as dyes from wastewater. Dyes are coloured compounds suitable for colouring textiles, wool, leather, paper and fibres. Natural dyes such as indigo have been in use for over 5000 years. Synthetic dyes have replaced natural dyes because of their low cost and vast range of new colours (Gabriel and Hong, 2008; Wenhong *et al.*, 2011). Today, there are more than 10,000 dyes with different chemical structures available commercially. Effluents of textile, paper and pulp, paint, printing and cosmetic industries contain significant amount of these dyes and must be treated to bring down their concentration to permissible limit before discharging into water bodies as required by environmental regulation act. The high solubility of dyes in water results in their wide dissemination into the environment, thus making them detrimental to crops, aquatic life and human health (Zhao *et al.*, 2011).

Consequently, several technological efforts have been made for cationic dyes removal from textile wastewater. Chemical and biological techniques have been most commonly used. The chemical oxidation has been applied mostly for colour wastewater treatment including chlorine, Fenton's

reagent, hydrogen peroxide, potassium permanganate or ozone as well as UV assisted activation (Gupta and Suhas, 2009). The biological methods involve the application of fungi, bacteria and algae to the dye wastewater treatment. The limiting factors of all the aforesaid dye wastewater treatment techniques are the high cost, large quantity of sludge generation, specificity to dye and require a combination of more than one process (Nandi *et al.*, 2009; Sarayu and Sandhya, 2012; Papita, 2010). Therefore, it is imperative to look for lower cost dye treatment solutions where the adsorption technique can be a viable option for the dye removal.

Increasing occurrence of many synthetic and natural organic substances in natural water led to the importance of using adsorption technique as one of the most effective methods of removing impurities from wastewater, because several dyes and their degradation (by-) products are toxic to living organisms. Therefore, removal of dyes is an important aspect of wastewater treatment before discharge, as it is difficult to remove dyes from effluent because they are not easily degradable and are generally not removed from wastewater by the conventional wastewater purification systems (Abd El-Latif *et al.*, 2010). The low-cost waste materials and agricultural based adsorbents have been investigated for a long time. The adsorbents used for cationic dyes treatment, include the Annonasquoma seeds, grass waste, sugarcane, AC-pine wood, AC-green pea peels, peanut shells, AC-cashew nut shells, etc. (Kumar *et al.*, 2011; Gupta *et al.*, 2016).

Peanut shell is a carbonaceous, fibrous solid waste which encounters disposal problem and is generally used for its fuel value. It is an agricultural solid waste that has been used as an adsorbent by Malik *et al.* (2007) for the removal of Malachite green from aqueous solution. The material is largely available and can be used as a potential adsorbent due to its physico-chemical characteristics and low cost. Peanut shell is easily available at zero prices.

Bentonite clay on the other hand has excellent rheological and adsorbent property. Since opposite charges attract, the negatively charged surface lattice of the bentonite clay may have an affinity for cationic dye. Thus, it could be assumed that bentonite clay may have a greater capacity to absorb cationic dye as it exhibited high removal of cationic dye such as malachite green (Irvan, 2019).

Mall *et al.* (2005) carried out a study on the effect of the contact time on the removal of methylene blue from aqueous solutions using acid-activated Algerian bentonite. The study revealed that the methylene blue adsorption was fast at the initial stage of the contact period, but became slower near equilibrium (120th–200th minutes). This phenomenon was due to the fact that a large number of vacant surface sites were available for adsorption at the initial stage. The remaining surface sites were difficult to occupy close to equilibrium, due to the slow pore diffusion of the solute molecules on the solid and the bulk phase. The increase of the initial concentration resulted in substantial increase in the amount of dye retained for the same quantity of bentonite, leading to increase in the amount of methylene blue molecules adsorbed onto the free sites available on the surface of clay particles. However, when all the sites were occupied, the amount of methylene blue molecules adsorbed became constant and there was formation of a monolayer.

In a study carried out by Toor and Jin (2012), natural bentonite, modified by thermal activation, acid activation and combined acid and thermal activation was used for the removal of diazo dye. The Congo Red adsorption increased with increase in contact time, with >95% dye removal attained using modified bentonites in 6 hours. The adsorption rate was very high in the first 2 hours, leading to 96.65, 92.75 and 91.62% of Congo Red removal using bentonite modified by acid and thermal activation, acid activation and thermal, respectively. On comparing these results to those of raw bentonite, approximately 20% Congo Red removal was enhanced by the acid and thermal activation and acid activation bentonites in 4 hours.

Lian *et al.* (2009) studied the adsorption of Congo Red (CR) from aqueous solutions onto Ca-bentonite. The removal efficiency of Congo Red onto Ca-bentonite by adsorption was initially rapid and slowed down gradually until it attained equilibrium. The effect of contact time on the percentage of colour removal at various temperatures examined at 100 mg L⁻¹ concentration of Congo Red showed that the contact time for Congo Red was 480 minutes when the temperatures were between 20

and 40°C. However, the uptake was very rapid and attained equilibrium in 180 minutes at 50°C, achieving maximum percent removal of 95.92% at 50°C. Increase in temperature led to increased uptake of Congo Red by Ca-bentonite, implying that the enthalpy change had positive values and the adsorption process was endothermic.

2.0. Methodology

The following apparatus were used for this study: analytical balance, mesh sieve (0.2micrometers), spatula, cylinder (10 ml, 50 ml and 100 ml), Erlenmeyer flask (250 ml), pH metre, beakers (50 ml, 100 ml, 250 ml and 1000 ml), funnel, 1 liter bottle, 1 yard of cotton cloth, Whatman filter paper (102 mm, 150 mm and 24 cm), storage bottles, foil paper, timer, magnetic stirrers, Scanning Electron Microscope (SEM) Hitachi S-3400N, Fourier Transform Infrared Spectrophotometer (FTIR), Ultra-violet Spectrometer PG instruments T80+, dropper pipette, masking tape, gloves, hot plate - IKA RCT basic, scissors and stirring rod.

2.1. Preparation of adsorbent

The natural waste were first washed with water to remove the dirt and then dried at room temperature. The dried peanut shell and bentonite clay was grinded to fine powder, sieved to obtain fine particle sizes and stored in glass containers. Less than 0.1 g of each sample i.e. peanut Shell, bentonite Clay and its combination were coated with a carbon tape placed on the SEM/EDX sample holder. The operation range was selected at 10 kV while the magnification required for the imaging was selected under a vacuum at 63µm for peanut shell, 71µm for bentonite clay and 71µm for the combination of the two.

2.2. Preparation of adsorbate

1000ml of water was boiled at 100°C, 3g of both dye and caustic soda was added to the water, it was stirred thoroughly. 1 yard of a cotton material was dipped into the dye solution and allowed for 20 minutes to absorb the dye and later removed and allowed to dry. The waste water was stored in a bottle for 3 days at room temperature before the experiment.

2.3. Batch adsorption experiments

2.3.1. Effect of adsorbent dose

0.5, 1.0, 1.5, 2.0, 2.5 g of the adsorbent were weighed and placed in flasks containing 30 mL of the dye waste water, a magnetic stirrer was dropped into each flask and the suspensions were stirred for 30 minutes. After agitation, the suspensions were filtered using a 180 mm Whatman filter paper.

2.3.2. Effect of contact time

For the second run, the agitation time was varied from 20 minutes to 100 minutes. 1 g of the adsorbent was added into a conical flask containing 30 mL of the dye solution for the different time ranges. After the time had elapsed, the suspension was filtered and the concentration determined.

2.3.3. Effect of pH

The effect of initial pH of dye solution on the percentage removal of malachite green dye was studied by varying the initial pH under constant process parameters. The pH was varied between 3 and 11 ppm, 0.1 g of the adsorbent was added to a conical flask containing 30 mL of the dye solution. 5 flasks containing malachite green dye at different pH ranges were used. The suspension was filtered and the concentration of the filtrate was determined using a UV-Visible Spectrophotometer. The pH was adjusted using 0.1M Hydrochloric Acid Solution and 0.1M Sodium Hydroxide Solution. In the end, the % removal was determined using the equation:

$$\% \text{Removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

Where C_0 is the initial concentration and C_e is the final concentration of adsorbate in the solution.

3.0. Results and Discussions

3.1. Characterization of adsorbent

3.1.1. Scanning Electron Microscope (SEM):

The output of the Scanning Electron Microscope (SEM) was images depicting fibre structures with pores various sizes. The SEM images of the adsorbents are shown in Plates 1 to 3.

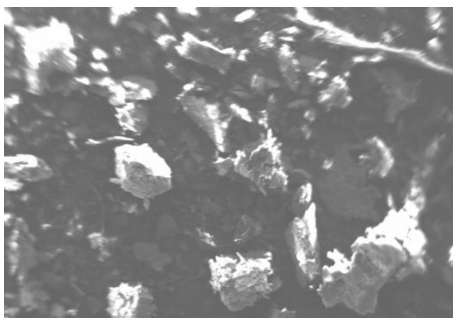


Plate 1: SEM image of peanut shell before dye adsorption

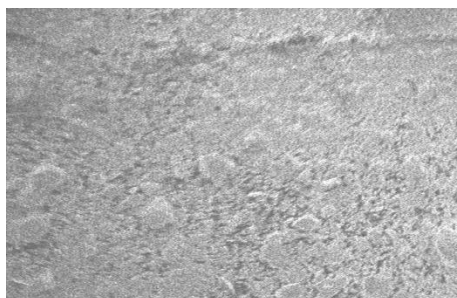


Plate 2: SEM image of bentonite clay before dye adsorption

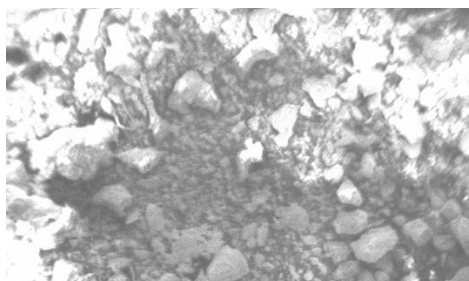


Plate 3: SEM image of peanut shell and bentonite clay before adsorption

The images revealed a fibre structure and showed a partial linkage among the fibres of the peanut shell which creates pores with different sizes and the bentonite clay has high swelling, sealing abilities, cation exchange and capacity for strong adsorption.

The SEM images of the adsorbents after adsorption of dye are shown in Plates 4 to 6. The images appear smoother and less porous because of the adsorption of colours, the surface was covered with dye molecules and samples were much more homogeneous.

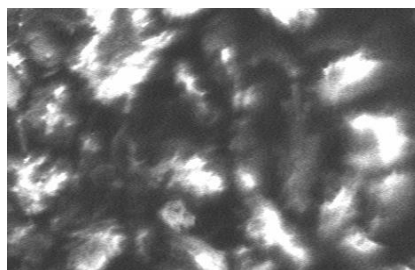


Plate 4: SEM image of peanut shell after dye adsorption

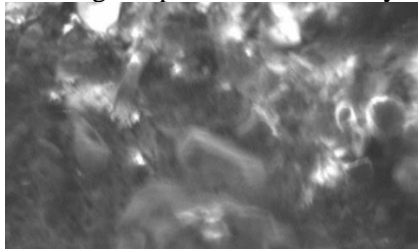


Plate 5: SEM image of bentonite clay after dye adsorption

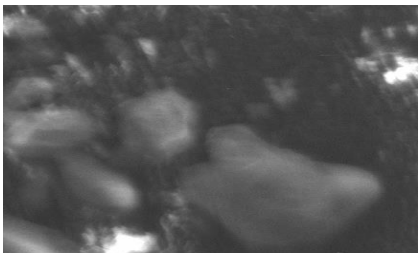


Plate 6: SEM image of both peanut shell and bentonite clay after dye adsorption

3.1.2. Electron Dispersive X-ray Spectroscopy (EDX):

The output of the EDS was a spectrum depicting the various elements present in the samples in form of peaks as shown in Figures 1 to 3.

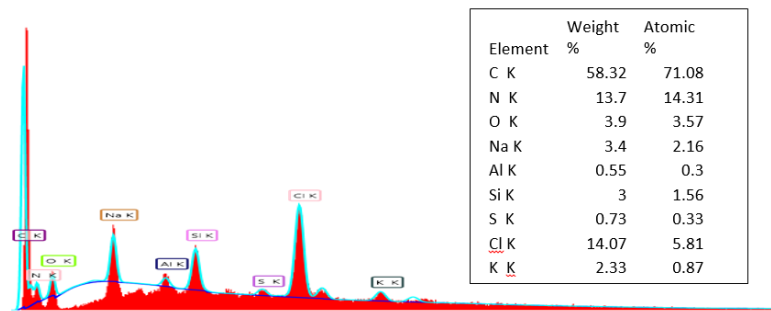


Figure 1: EDX image of peanut shell before dye adsorption

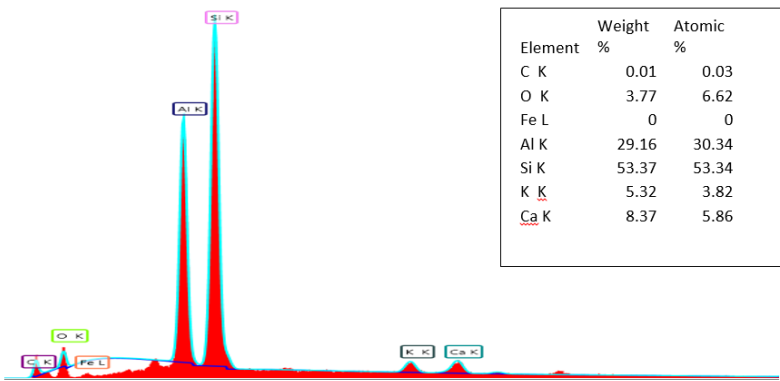


Figure 2: EDX image of bentonite clay before dye adsorption

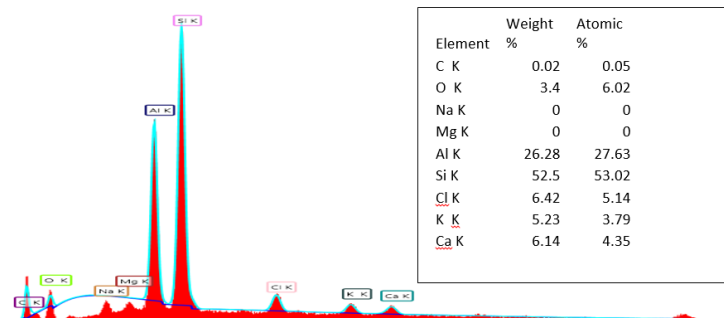


Figure 3: EDX image of peanut shell and bentonite clay before dye adsorption

From the images in Figure 1 to 3, the samples showed visible amounts of carbon, oxygen which are important for adsorption also containing nitrogen ,calcium ,aluminum ,silicon, etc. The highest peaks in the images depict the strongest adsorption capacities.

From the images in Figure 4 to 6, carbon and oxygen were found but reduced in weight because it was used to absorb the dye likewise the remaining compounds were all reduced in weight.

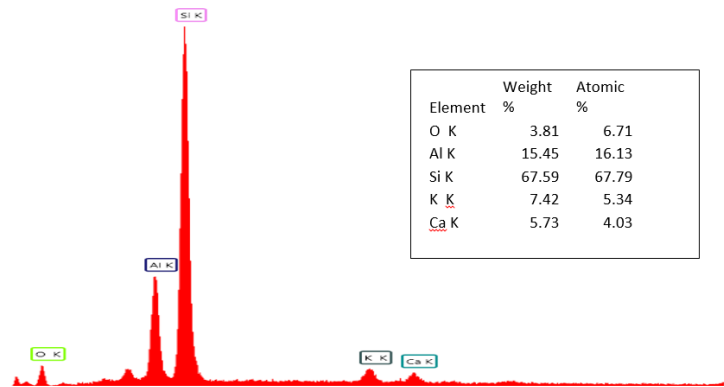


Figure 4: EDX image of peanut shell after dye adsorption

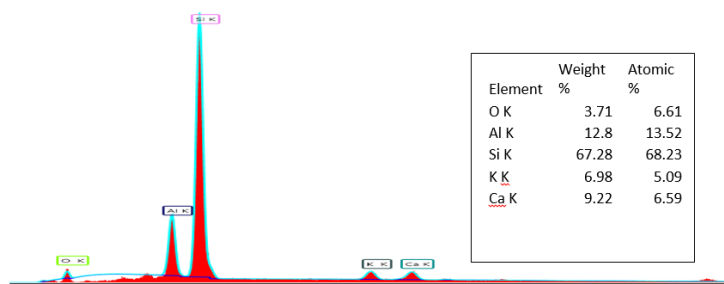


Figure 5: EDX image of bentonite clay after dye adsorption

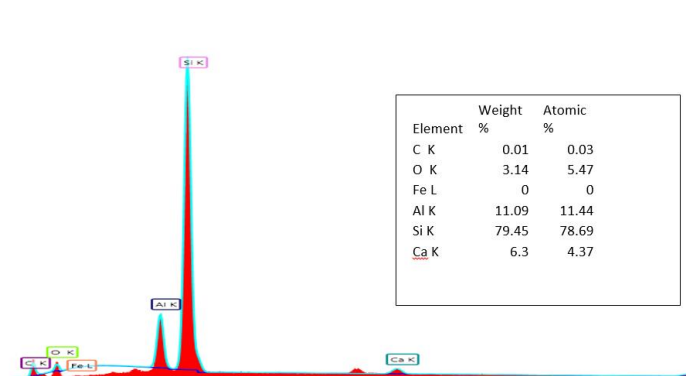


Figure 6: EDX image of peanut shell and bentonite clay after adsorption

3.1.3. Fourier Transform Infrared (FTIR) spectrophotometric analysis:

For the FTIR analysis, only the peaks between 1500 cm^{-1} and 4000 cm^{-1} were studied as that is the functional group region, while any peaks below 1500 cm^{-1} belong to the fingerprint region which we are not interested in. The plots are shown in Figures 7 to 12.

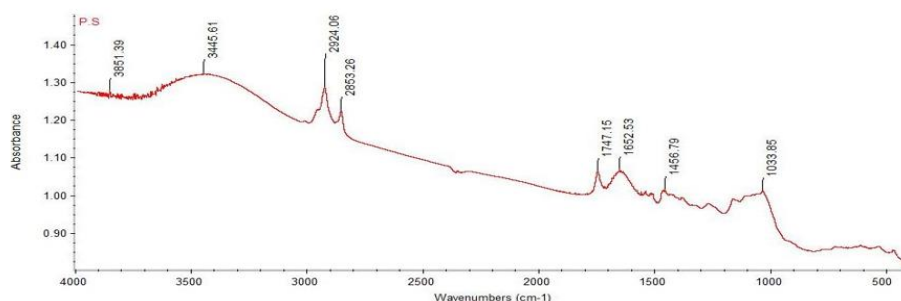


Figure 7: FTIR of peanut shell before dye adsorption; it shows peaks at 3851 with functional group O-H, 3445.61 N-H, 2853.26-2924.06 C-H 1747.15 C=O, 1652.52 C=C

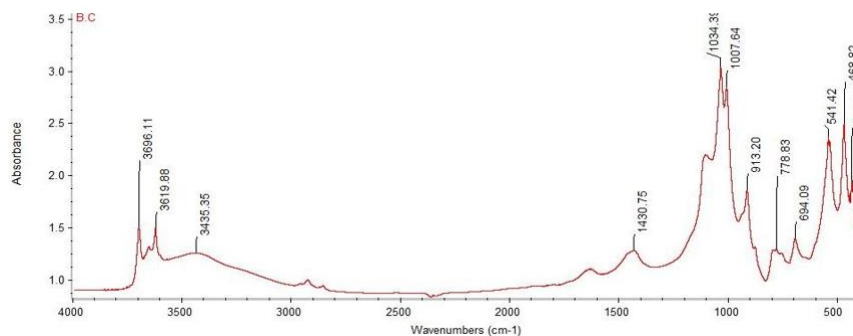


Figure 8: FTIR of bentonite clay before dye adsorption; Peaks from 3,696.11-3,619.88 O-H, 3,435.33 N-H

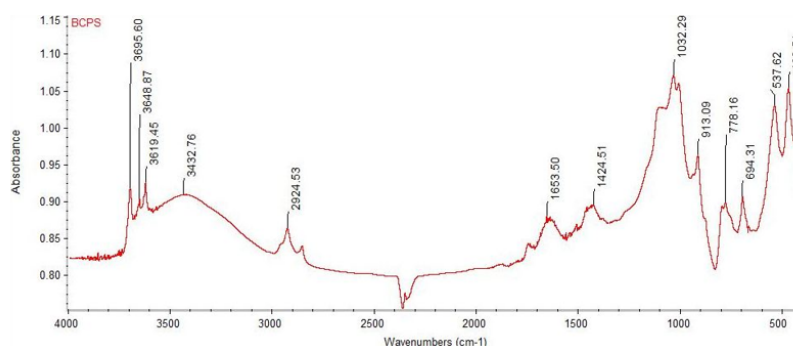


Figure 9: FTIR of peanut shell and bentonite clay before dye adsorption; Peaks from 3,695.60-2924.52 O-H, 3432.76 N-H 1653.50 C=C

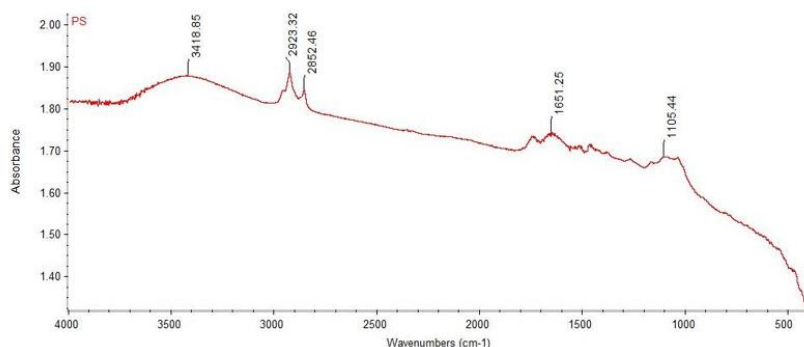


Figure 10: FTIR of peanut shell after dye adsorption; Peaks at 3428.85 O-H, 2923.32-2852.46 O-H 1651.25 C=C

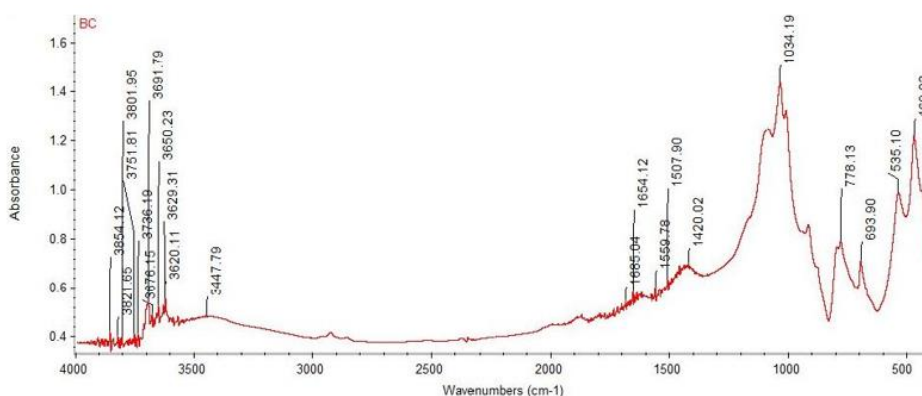


Figure 11: FTIR of bentonite clay after dye adsorption; Peaks at 3854.12-3620.11 O-H, 3447.79 N-H, 1685.04-1654.12 C=O, 1559.79-1507.90 C=C

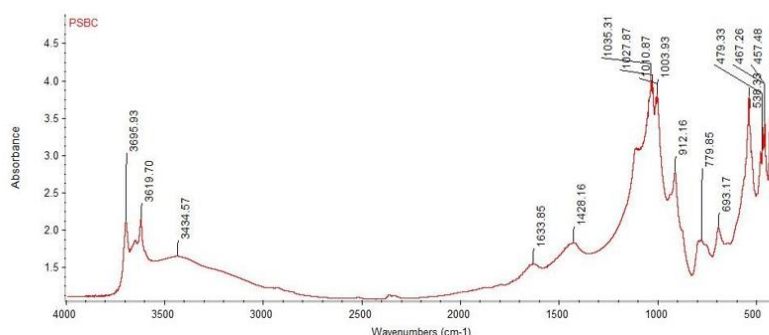


Figure 12: FTIR of peanut shell and bentonite clay after dye adsorption; Peaks at 3,695.93-3619.70 O-H, 3434.57 N-H, 1633.85 C-N

From the images in Figures 7 to 12, the FTIR shows C=C which is a functional group and indicate property of a good adsorbent; it also showed some functional groups like O-H, N-H, C-H, N-H, etc.

3.2. Analysis of physico-chemical properties of the adsorbent

3.2.1. Effect of adsorbent dose:

The effect of adsorbent dose on malachite green was investigated as shown in Figure 13. From the figure below peanut shell showed the absorbance increased from the first dose and not much increase from second dose to the forth and high increase on the last dose. For bentonite clay from the second dose to the forth dose no much increase and decrease at the last dose. The composite of both peanut

shell and bentonite clay there was reasonable increase from the first to the last dose. Numerically, there was 31.5% increase in absorbance for peanut shell, 80% increase for the composite and 27% increase for the bentonite when adsorbent load increases from 0.5g to 2.5g. This shows highest absorbance for the composite.

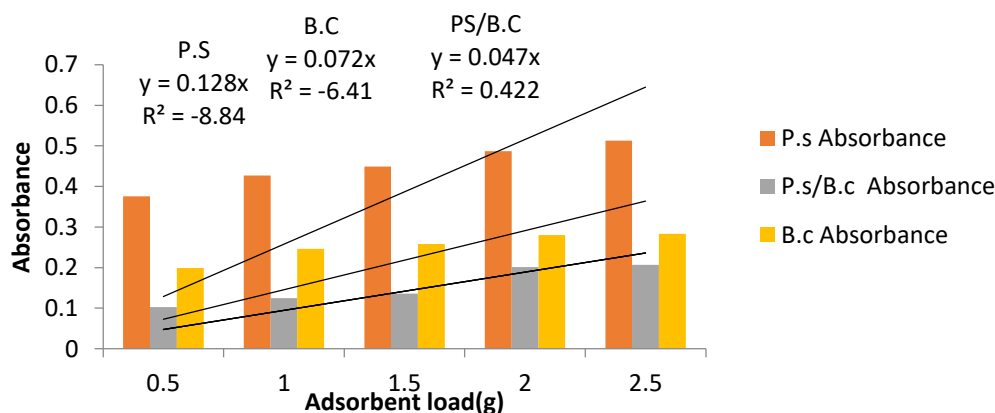


Figure 13: Effect of Adsorbent dose

3.2.2. Effect of contact time:

Figure 14 shows that for peanut shell there was increase from 20-40 minutes, no visible increase from 40-60 minute but increase from 60-100 minutes. For bentonite clay there was increase from 20-60 minutes no visible increase from 60-80 minutes and decrease from 80-100 minutes. For the composite of peanut shell and bentonite clay there was increase from 20-40 minutes then decrease from 40-80 minutes and increase from 80-100 minutes in absorbance. Although

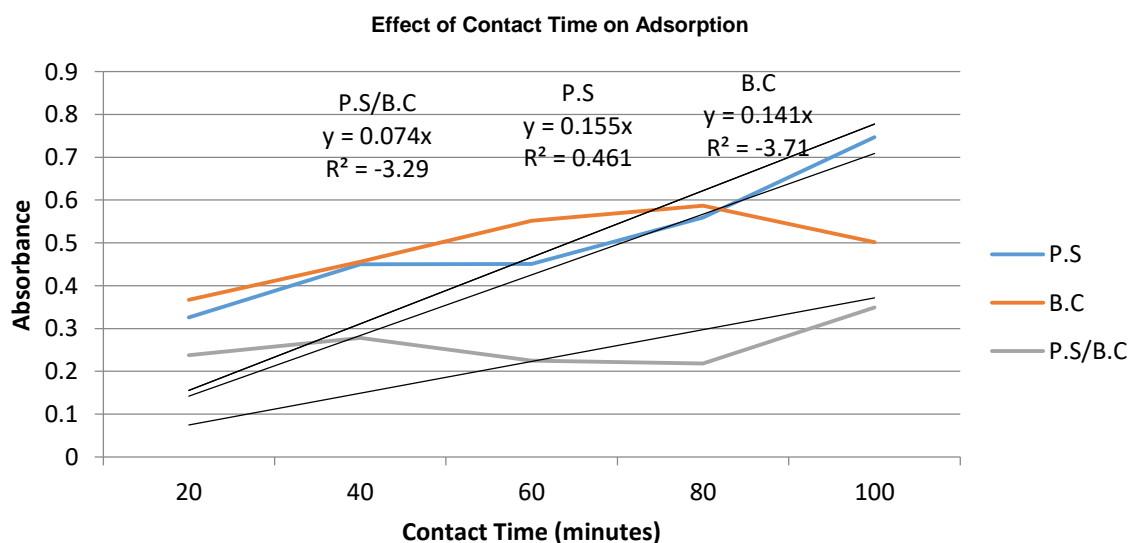
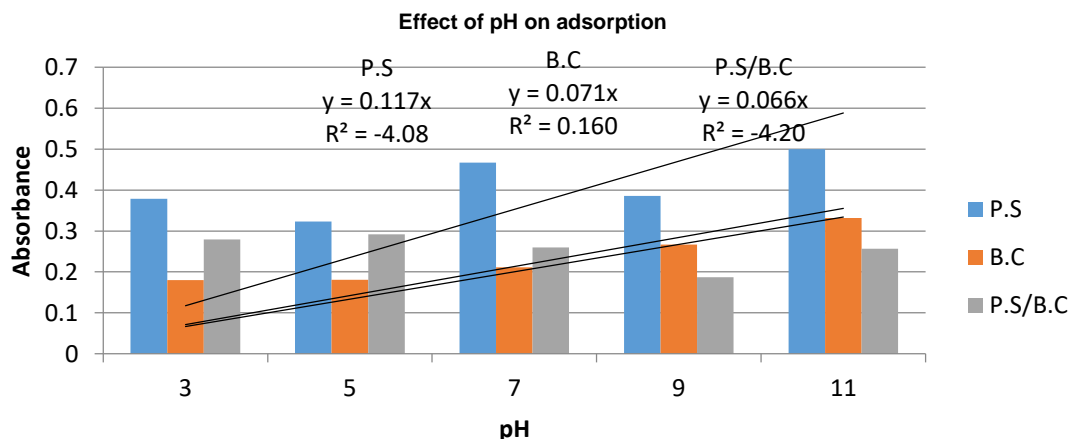


Figure 14: Effect of contact time

3.2.3. Effect of pH:

Figure 15 of pH for peanut shell shows a decrease in absorbance on the acidic, increase at neutral state, decrease at the basic and slight increase at the last lap. For the bentonite clay it had low absorbance at the acidic stage then increased a bit at neutral to basic stage. Lastly for combination of peanut shell and bentonite clay shows a decrease on the acidic stage down to the neutral basic stage but slightly increased at the tail end. It is revealed that Peanut shell has the highest absorbance at pH 11, also for bentonite clay, the highest absorbance was at 11 however for the composite, the highest was at 5. With increase in pH both Peanut shell and bentonite clay had absorbance increased as it can be seen that peanut shell and bentonite clays' absorbance increase 38% and 88% respectively from pH 3 to pH 11.

**Figure 15: Effect of pH**

P.S = Peanut shell, B.C = Bentonite clay and P.S/B.C = the composite of the peanut shell and the bentonite clay

4.0. Conclusions

Removal of dye from industrial wastewater from aqueous solutions by adsorption with natural waste i.e. peanut shell, bentonite clay and its composite has been experimentally determined and the following observations are made:

- SEM showed visible pores sites enabling pore diffusion and adsorption of dye into the active pore sites.
- FTIR showed the functional group of $C=C$ which is a good property for adsorbent in the all the samples.
- EDX showed the elemental composition of the samples. Elements like carbon, oxygen which are basic were seen and were later adsorbed after the process which showed less weight. Other compounds like nitrogen, calcium needed in both peanut shell and bentonite clay were present too, aluminium, silicon, e.t.c.
- Some physical parameters were taken into consideration and showed visible results, the adsorption rate increase with increase in the adsorbent load.
- The contact time for adsorption was seen to increase for peanut shell all through the 1 hour 40 minutes; it was ran for the bentonite clay, adsorption decreased towards the last lap and the composite had increase at the beginning but decrease at the end. At 60-80 minutes optimal time was achieved due to saturation of active sites for high removal of dye efficiency.
- pH varies here for the peanut shell; there was increase as the pH was increase from the acidic to the neutral side but decreased at the basic side. In respect of the bentonite clay, there was decreased as the pH increased towards neutral and basic side. Lastly the composite the pH decreased at the acidic to neutral but slightly increase at the basic side. We can say that for the peanut shell and bentonite clay pH was increased at the acidic side which gives the best adsorption than the composite. This reveals that the two adsorbents performed better than the composite.
- Concentration analysed showed increase in the absorbance as the concentration increased. It was seen that Peanut shell %removal was 69.07% while bentonite clay was 70.73% and the combination showed 69.05%.

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